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(71)Applicant : SEKISUI CHEM CO LTD

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(72)Inventor : MIYASHITA HIROSHI

(54) PRODUCTION OF PRESSURE-SENSITIVE ADHESIVE TAPE

(57)Abstract:

PURPOSE: To produce a pressure-sensitive adhesive tape having sufficiently high initial tack to an adherend and peelable through heat treatment, by applying a photopolymerizable composition consisting of an acrylate monomer, a tackifier resin, etc., to one side of a specified synthetic resin film or sheet and irradiating it with light.

CONSTITUTION: An uncured or semicured photopolymerizable composition consisting of an acrylate monomer, a vinyl monomer copolymerizable therewith, a tackifier resin, a cross-linking agent and a photopolymerization initiator is applied to at least one side of a synthetic resin film or fibrous sheet having a heat shrinkage of 5-80% and then is polymerized by irradiation with light. As the resin film, a uniaxially or biaxially oriented film of, e.g. a polyester, polystyrene, polyvinyl chloride, polypropylene or polyethylene is used. Examples of the tackifier resin include a rosin resin, a terpene resin and a chroman-indene resin. It is desirable that the amount of the tackifier resin to be incorporated is 10-70 pts.wt. based on 100 pts.wt. of the monomers.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacture approach of the adhesive tape in which re-exfoliation is possible with heating.

[0002]

[Description of the Prior Art] Conventionally, in the time of paint of an automobile etc., it is used as a masking tape, and paint afterbaking can remove easily and the adhesive tape by heating aiming at planning **** of an activity in which re-exfoliation is possible is demanded.

[0003] That (publication-number 4-No. 88075 official report) in which the adhesive tape (Provisional Publication No. 60-252681) with which the binder layer which contains thermal-expansion nature resin on a base material sheet was prepared as adhesive tape of the above-mentioned purpose, and the binder layer which contains a foaming agent in the base material of heat shrink nature were prepared is reported.

[0004]

[Problem(s) to be Solved by the Invention] However, the above-mentioned adhesive tape had the low adhesion by ordinary temperature, and could not be used for the application aiming at the immobilization which requires a load, but was limited to masking, a label, etc.

[0005] Moreover, although there are a base material and an imprint method to stick the direct spreading method which applies a binder solution to a base material directly, and after making a binder layer once form on an exfoliation sheet when manufacturing such adhesive tape Although a binder solution must be heated in the thing of a direct spreading method in order to dry a solvent after coating, if the temperature of about 100 degrees C used for desiccation of a binder is usually applied, contraction of a base material will occur, and there is a problem referred to as that the function as a product is not obtained. Although heat does not start on the other hand in order to stick the binder layer made to form separately at a base material in the case of an imprint method, a man day increases compared with a direct spreading method, and there is a problem referred to as being unable to discover sufficient adhesion force (support nature) of a binder layer to that productivity is bad and a synthetic-resin film, or a fiber sheet. Furthermore, in the binder of a solvent mold, the adhesion rise after sticking on adherend was high, and the problem referred to as not suitable in the point called removability also had it.

[0006] The place which this invention was made in view of the above-mentioned trouble, and is made into the purpose is offering the approach of having adhesion sufficient in ordinary temperature, and manufacturing easily the adhesive tape in which re-exfoliation is possible by the direct spreading method about 100 degrees C by performing low-temperature heat-treatment comparatively.

[0007]

[Means for Solving the Problem] In this invention, the synthetic-resin film or fibrous sheet which has 5 - 80% of heating contraction is used. Here, heating contraction is contraction of the film area defined by the following formulas by leaving it for 10 minutes 100 degrees C.

Contraction (%) = [(die-length x width of face before heating) - (die-length x width of face after

heating)] $\times 100 / (\text{die-length} \times \text{width of face before heating})$

[0008] Since thermofusion of that to which removability will be lost if heating contraction of a synthetic-resin film or a fibrous sheet becomes less than 5%, and contraction exceeds 80% is carried out substantially, it cannot be used as a base material, but it is 30 - 80% preferably. As such a synthetic-resin film, one shaft or biaxial oriented films, such as polyester, polystyrene, a polyvinyl chloride, polypropylene, and polyethylene, are mentioned. Moreover, the textile fabrics or the nonwoven fabric which consists of the synthetic resin same as a fibrous sheet as the above is mentioned.

[0009] Although the thickness of the above-mentioned synthetic-resin film or a fibrous sheet should just be suitably selected by the application, its 10-200 micrometers are usually desirable in respect of the ease of using. The photopolymerization nature constituent used in this invention consists of an acrylate monomer, an acrylate monomer and a copolymerizable vinyl system monomer, a tackifier, a cross linking agent, and a photoinitiator.

[0010] As the above-mentioned acrylate monomer, for example, n - butyl (meta) acrylate, 2 - ethylhexyl (meta) acrylate, iso octyl (meta) acrylate, iso nonyl (meta) acrylate, etc. are mentioned.

[0011] Moreover, as an acrylate monomer and a copolymerizable vinyl system monomer, an acrylic acid (meta), acrylamide (meta), acrylonitrile (meta), N - permutation acrylamide, 2-hydroxyethyl (meta) acrylate, N - vinyl pyrrolidone, a maleic acid, an itaconic acid, N - methylol acrylamide, etc. are mentioned. It is desirable that copolymerization of the 50 - 99 % of the weight of the above-mentioned acrylate monomers and the 50 - 1 % of the weight of the above-mentioned vinyl system monomers is carried out.

[0012] Although rosin system resin, alicycle group saturated hydrocarbon resin, terpene resin, terpene phenol resin, aromatic series denaturation terpene resin, a carbon number 5 or 9 system petroleum resin, and cumarone indene resin are mentioned as the above-mentioned tackifier, it is desirable at the point that aliphatic series saturation hydrocarbon resin, terpene resin, terpene phenol resin, or cumarone indene resin makes initial adhesion high especially. The addition of the above-mentioned tackifier has desirable 10 - 70 weight section to the total quantity 100 weight section of the above-mentioned acrylate monomer and a vinyl system monomer.

[0013] It is for the above-mentioned cross linking agent constructing a bridge in an acrylate monomer, and an acrylate monomer and a copolymerizable vinyl system monomer, and giving cohesive force. JI (Tori) acrylate can be mentioned. Specifically For example, hexanediol di(metha)acrylate, Ethylene glycol di(metha)acrylate, PUROI (Pori) range (meta) acrylate, (Pori) Polyfunctional monomer, such as neopentyl glycol (meta) acrylate, pen TAERISURITORUTORI (meta) acrylate, dipentaerythritol hexa (meta) acrylate, the EPO SHIKIA chestnut rate, polyester acrylate, and urethane acrylate, is mentioned.

[0014] The addition of a cross linking agent has desirable 0.001 - 10 weight section to the above-mentioned acrylate monomer, an acrylate monomer, and the copolymerizable vinyl system monomer 100 weight section.

[0015] As a photopolymerization initiator which can be used for this invention, an acetophenone system, a benzoin ether system, a ketal system, a halogenation ketone system, and an acyl phosphino KISHIDO system can be mentioned. As an example of an acetophenone system, a 4 - (2 - hydroxy ethoxy) phenyl (2 - hydroxy - 2 - propyl) ketone and alpha - hydroxy - alpha and alpha' - dimethyl - acetophenone, methoxy acetophenone, 2, and 2 - dimethoxy - 2 - phenyl acetophenone etc. is mentioned, benzoin ethyl ether, benzoin iso-propyl ether, etc. are mentioned as an example of a benzoin ether system, and benzyl wood ether ketal is mentioned as an example of a ketal system.

[0016] The addition of the above-mentioned photopolymerization initiator is the point of a polymerization rate of reaction, and its 0.001 - 10 weight section is desirable to the above-mentioned acrylate monomer, an acrylate monomer, and the copolymerizable vinyl system monomer 100 weight section.

[0017] Furthermore, much more re-exfoliation effectiveness can be acquired by adding thermal-expansion nature resin, a foaming agent, etc. in the above-mentioned photopolymerization constituent. As thermal-expansion nature resin, a microsphere (a trade name, the Matsumoto fats-and-oils company make), Expancel (a trade name, product made from Expancel), SAMMAI cross fair (a trade name, Dow

Chemical Co. make), etc. are mentioned.

[0018] The addition of the above-mentioned thermal-expansion nature resin has desirable 3 - 40 weight section to the photopolymerization nature constituent 100 weight section. It is because initial adhesion will decline under in 3 weight sections if the improvement in the re-exfoliation effectiveness is hard to be obtained and 40 weight sections are exceeded.

[0019] As a foaming agent, for example Moreover, an ammonium carbonate, an ammonium hydrogencarbonate, A sodium hydrogencarbonate, ammonium nitrite, a sodium borohydride, The thing of the inorganic system represented by azides, azobis butyronitrile, an AZOJI carvone amide, Azo compounds, such as a barium azo dicarboxy rate, tosyl hydrazide, Diphenylsulfone -3, a - disulfo hydrazine, and 3 '4, 4'-oxy-screw (benzene sulfo hydrazide), Hydrazine system compounds, such as an allyl compound screw (sulfo hydrazide), rho-tolulene sulfonyl semicarbazide, Semicarbazide system compounds, such as a 4 and 4'-oxy-screw (benzenesulphonyl semicarbazide), 5-morphoryl - The thing of the organic system represented with N-nitroso compounds, such as triazole compound [, such as 1, 2, 3, and 4-thiatriazole,], N, and N'-dinitroso terephthalamide, etc. is mentioned.

[0020] Furthermore, a viscosity controlling agent may be added if needed. By adding a viscosity controlling agent 0.1 to 30% of the weight to the total quantity of the above-mentioned acrylate monomer, and an acrylate monomer and a copolymerizable vinyl system monomer, the viscosity of a photopolymerization nature constituent can be raised and the thickness formed at the time of spreading can be maintained. Consequently, it becomes easy to perform thickness adjustment of the binder layer formed after an optical exposure. As such a thing, Aerosil etc. is preferably mentioned by acrylic rubber and the inorganic system by the organic system.

[0021] With the light used by this invention, although electromagnetic waves, such as the light, ultraviolet rays, and an electron ray, can be mentioned, ultraviolet rays are usually preferably used from the point of reactivity and handling nature. Furthermore, the thing near 300-400nm has the most desirable wavelength also in an ultraviolet-rays field. Luminous intensity and an exposure should just be suitably chosen by the conditions of the class of photopolymerization nature constituent, thickness, and others.

[0022] Although especially the thickness of the binder layer formed by [above-mentioned] carrying out an optical exposure is not limited, its 10-100 micrometers are usually desirable from the ease of using as adhesive tape.

[0023] Although the approach of imprinting on the above-mentioned film or a fibrous sheet is once mentioned as an approach of applying the above-mentioned photopolymerization nature constituent to the synthetic-resin film or fibrous sheet of heating shrinkage characteristics the approach of carrying out direct coating, or after applying on an exfoliation sheet, the direction which carries out direct coating in this invention which does not require heat is the point of productivity, and much more advantage can be harnessed.

[0024] Furthermore, after applying a photopolymerization nature constituent on the exfoliation sheet of transparency also in the coating approach by imprint, an optical exposure is once carried out. the method of making a binder layer form is also possible if needed by considering as the photopolymerization nature constituent of the semi-hardening condition which carried out the until polymerization to some extent, sticking this photopolymerization nature constituent side on the above-mentioned film or a fibrous sheet, carrying out an optical exposure from an exfoliation sheet tooth-back side further, and completing a polymerization completely.

[0025] Since the oxygen in atmospheric air usually checks a polymerization as conditions which advance the above-mentioned photopolymerization reaction, it is desirable to be carried out, the bottom of an inert gas ambient atmosphere or where the detachability film which penetrates light is stuck on a photopolymerization nature constituent spreading side.

[0026]

[Function] Since the base material of the adhesive tape obtained by this invention is the synthetic-resin film or fibrous sheet which has 5 - 80% of heating contraction, a base material layer can be shrunk by heating. Moreover, since a binder layer is formed by carrying out the optical exposure of the

photopolymerization nature constituent which consists of an acrylate monomer, an acrylate monomer and a copolymerizable vinyl system monomer, a tackifier, a cross linking agent, and a photopolymerization initiator under coincidence existence, compared with a solvent mold binder, the tackifier is distributed by the binder layer at homogeneity, and it has high initial adhesion also in a room temperature, and there is no adhesion rise. Consequently, by heating, a base material layer can contract and adhesive tape can be exfoliated from adherend.

[0027]

[Example] Hereafter, the example of this invention is explained.

(Examples 1-3) the 2-ethylhexyl acrylate 82 section (the weight section --) Like the following, the N-vinyl-pyrrolidone 8 section, the carboxyethyl acrylate 10 section, The cumarone-indene-resin (Nippon Steel chemistry company make, S crystal A-120S) 15 section, the hexanediol diacrylate 0.06 section, the acrylic rubber 2.5 section, and 4-(2-hydroxy ethoxy) phenyl (2-hydroxy-2-propyl) ketone (the Merck Co. make --) The photopolymerization nature constituent which consists of the DAROKYUA 2959 1.3 section was applied to 50-micrometer thickness on one side of the polyester film which has transparency by detachability, 15mW ultraviolet rays were irradiated for 30 seconds under nitrogen-gas-atmosphere mind, and the photopolymerization nature constituent of a semi-hardening condition was obtained.

[0028] heating contraction in 100 degrees C laid the photopolymerization nature constituent side of polyester film in which the photopolymerization nature constituent of the acquired semi-hardening condition was formed on top of the polyester film (the Toyobo Co., Ltd. make and a tooth space -- clean) of 40 - micrometer thickness they are [thickness] 67 and 74 or 35%, respectively, ultraviolet rays were again irradiated for 120 seconds from the polyester-film side which has transparency by the above-mentioned detachability, by carrying out a polymerization completely, the binder layer was made to form and adhesive tape was obtained. Each was made into the example 1, the example 2, and the example 3.

[0029] The 2 - ethylhexyl acrylate 82 section, the N - vinyl-pyrrolidone 8 section, (Example 4) the carboxyethyl acrylate 10 section and bear loin DIN resin (the Nippon Steel chemistry company make --) The S crystal A-120S15 section, the hexanediol diacrylate 0.06 section, the acrylic rubber 2.5 section and 4-(2-hydroxy ethoxy) phenyl (2-hydroxy-2-propyl) ketone (the Merck Co. make --) Heating contraction in 100 degrees C the photopolymerization nature constituent which consists of the DAROKYUA 2959 1.3 section 74%, applied to 50-micrometer thickness, and irradiated 15mW ultraviolet rays for 120 seconds under nitrogen-gas-atmosphere mind, the binder layer was made to form on one side of the polyester film (the Toyobo Co., Ltd. make and a tooth space -- clean) of 40-micrometer thickness, and adhesive tape was obtained.

[0030] (Example 5) Except that heating contraction used the textile-fabrics sheet (the Teijin, Ltd. make, TEBIRON fiber) of the polyvinyl chloride fiber of 40-micrometer thickness 70% instead of the polyester film of heating shrinkage characteristics used in the example 1, adhesive tape was obtained completely like the example 1.

[0031] (Example 6) Adhesive tape was further obtained like the example 1 to the photopolymerization nature constituent used in the example 1 except having added the thermal-expansion nature resin (Matsumoto fats-and-oils company make, microsphere F-30) 10 section.

[0032] (Example 1 of a comparison) Applied to one side of the polyester film of heating shrinkage characteristics which used the acrylic binder solution (SK dyne 1700, Soken Chemical & Engineering make) in the example 1, carried out stoving for 20 minutes at 60 degrees C, the 50-micrometer binder layer was made to form, and adhesive tape was obtained.

[0033] (Example 2 of a comparison) Applied to one side of the polyester film of heating shrinkage characteristics which used the binder solution of the toluene which becomes the acrylic binder solution (Soken Chemical & Engineering make, SK dyne 1700) 100 section from the thermal-expansion nature resin (Matsumoto fats-and-oils company make, microsphere F-30) 10 section in the example 1, and carried out stoving for 20 minutes at 60 degrees C, the 50-micrometer binder layer was made to form, and adhesive tape was obtained.

[0034] (Example 3 of a comparison) Adhesive tape was obtained by the completely same approach as

the example 2 of a comparison except having made thermal-expansion nature resin (the Matsumoto fats-and-oils company make, microsphere F-30) into the 30 sections in the example 2 of a comparison. Each adhesive tape obtained in the above-mentioned example and the example of a comparison was cut on 20x100mm square, and it stuck on the ABS-plastics plate, and was stuck by pressure with 2kg roller. Then, after leaving it for 30 minutes in the adhesion after leaving it for 30 minutes in ordinary temperature, and ordinary temperature, the direction exfoliation force (g/20mm) of 180 degrees from the ABS-plastics plate after heating for 10 minutes in 100 more-degree C oven was measured according to JIS-Z0237, respectively, and adhesion evaluation after initial adhesion and heat-treatment was performed.

[0035] Furthermore, after sticking on the ABS-plastics plate each adhesive tape obtained in the example and the example of a comparison as the another evaluation approach of removability and being stuck by pressure with 2kg roller, evaluated the self-weight fall nature when turning adhesive tape to the bottom and leaving it for 10 minutes in 100-degree C oven, what fell was made into O, and what did not fall was made into x. The above evaluation result was shown in Table 1.

[0036]

[Table 1]

粘着力	実施例						比較例		
	1	2	3	4	5	6	1	2	3
常温時 (g/20mm)	1300	1300	1300	1300	1300	1100	1300	800	400
100 °C加熱後 (g/20mm)	600	350	800	600	300	400	2000	500	100
自重落下性	○	○	×	○	○	○	×	○	○
粘着剤製膜 時間 (分)	2.5	2.5	2.5	2.5	2.5	2.5	20	20	20

[0037]

[Effect] The adhesive tape of the initial adhesion over adherend obtained by the approach of this invention is fully expensive, by performing 100-degree C heat-treatment, adhesion can fully be dropped and the adhesive tape in which re-exfoliation is possible can be obtained. Moreover, since it becomes very shorter than the case where the time amount taken to form a binder layer uses the usual solvent mold binder according to the approach of this invention, productivity will also become high. In case adhesive tape is furthermore manufactured, since that heat starts making a binder layer form does not have **, direct coating can be made a base material. Therefore, manufacture of the adhesive tape in which the re-exfoliation with high productivity is possible is attained.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the adhesive tape characterized by carrying out an optical exposure at least at it after applying to the whole surface the photopolymerization nature constituent which consists of as copolymerizable the vinyl system monomer of the synthetic-resin film which has 5 - 80% of heating contraction, or a fibrous sheet as un-hardening or the acrylate monomer of a semi-hardening condition, and an acrylate monomer, a tackifier, a cross linking agent, and a photopolymerization initiator.

[Translation done.]